



Hydrogen generation from catalytic hydrolysis of sodium borohydride by a novel Co(II)–Cu(II) based complex catalyst

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H I G H L I G H T S

- Co(II)–Cu(II) supported salicylaldimine derivatives complex catalysts were prepared.
- The catalysts were tested for hydrogen generation from hydrolysis of NaBH₄.
- Co(II)–Cu(II) ratio, NaBH₄, NaOH, temperature and catalyst amount effects were investigated.
- The optimal mixture percentage of Co(II)–Cu(II) catalyst was 60:40.
- These catalysts were characterized via XRD, FT-IR and SEM techniques.

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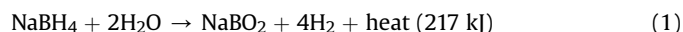
In the present work, Co(II)–Cu(II) supported salicylaldimine derivatives complex catalysts and their mixtures are tested for hydrogen generation from the hydrolysis reaction of sodium borohydride (NaBH₄). The hydrolysis of NaBH₄ with Co(II)–Cu(II) supported complex catalysts is investigated depending on the Co(II)–Cu(II) ratio, NaBH₄ concentration, NaOH concentration, temperature and catalyst amount. The results suggested that the optimal mixture percentage of Co(II)–Cu(II) catalyst is 40:60. The obtained complex catalysts are characterized by XRD, FT-IR and SEM techniques and evaluated for their activity for the hydrogen generation from the hydrolysis reaction of NaBH₄.

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1. Introduction

The current global economy is largely dependent on fossil fuels. In recent years, hydrogen has attracted much attention as an alternative energy carrier to replace fossil fuels due to its clean, renewable, and non-polluting nature [1–4]. The current commercial production of hydrogen requires fossil fuels as feed material. Hydrogen production is a large and growing industry. In the past few years, complex hydrides have been demonstrated to be promising hydrogen sources for portable application. NaBH₄ is very stable, non-flammable, non-toxic in nature, and able to store hydrogen with capability of 10.8 wt%. Therefore, there is a growing interest in hydrogen generation using NaBH₄ [5–7]. The efficiency of hydrogen release by using suitable catalysts can be significantly

enhanced. Schlesinger et al. [8] show that the hydrogen generation from alkaline NaBH₄ solution could accelerate via the following reaction:



The rate of hydrogen generation from self-hydrolysis of NaBH₄ is not satisfactory at room temperature. Therefore, the use of a catalyst plays a key role in hydrogen generation from the NaBH₄ solution. In order to accelerate the rate of hydrogen generation from hydrolysis of NaBH₄ with various catalysts such as Ruthenium supported catalyst [6,9–13], cobalt (Co) supported catalyst [14–18], nickel (Ni) based catalyst [19], Co–Ni catalyst [20], Ni–B catalyst [21], Ni–CoB catalyst [22], copper (Cu)–Co catalyst [23], Co–Cu–B catalyst [7] Pd, Pt–Ru, Pt–Pd alloys [24–26], etc. have been developed. However, only a few studies on the application of complex catalysts to hydrogen production have been reported [27–34].

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In addition, the catalytic activities of the metalphthalocyanine derivatives complexes have not been investigated for hydrogen production from hydrolysis of NaBH_4 solution.

The cost and availability of catalyst in the process hydrogen generation from hydrolysis of NaBH_4 with various catalysts are predominantly parameters. The high cost of the catalysts restricts their broad application. Cu-based catalysts have gained attention as catalyst because they are cheaper and more environmentally friendly. Thus, if Cu-based catalysts can overcome the limitation of low activity, they could prove invaluable [35].

In this work, we describe the synthesis of a new 4-4'-methylene bis(2,6-diethyl)aniline–3,5-di-tert-butylsalicylaldimin ligand (MA:742) by the reaction of 4-4'-methylene bis(2,6-diethyl)aniline and corresponding Cu(II) and Co(II) metal complexes. The basic aim of this study is to develop a feasible new catalyst system for hydrogen generation by catalytic hydrolysis of NaBH_4 . The effects of complex catalyst, NaBH_4 concentration, NaOH concentration, catalyst amount, Co(II)–Cu(II) ratio in complex mixture and temperature on the rate of hydrolysis were investigated. The catalyst system was characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD).

2. Materials and methods

For the convenience of the reader, the compounds and proposed structures are shown in Figs. 1 and 2. FT-IR spectra were recorded as KBr pellets on a Perkin–Elmer FT-IR spectrometer in the range $4000\text{--}450\text{ cm}^{-1}$. XRD data are collected on an STOE IPDSII image plate detector using Mo $K\alpha$ radiation ($\lambda = 0.154184\text{ nm}$) from a suitable single crystal mounted on a glass fiber. The SEM measurements were carried out on a Zeiss Evo 50 Series.

2.1. Synthesis of the salicylaldimine ligands

All chemicals were of analytical reagent grade and purchased from Sigma or Merck 4-4'-methylene bis(2,6-diethyl)aniline–3,5-di-tert-butylsalicylaldimin ligand was synthesized by the reaction of 2.0 mmol 4-4'-methylene bis(2,6-diethyl)aniline in 30 mL absolute ethanol with 1.0 mmol 3,5-di-tert-butylsalicylaldimin, according to the similar method reported in the literatures [36,37]. In addition, 3–4 drops of formic acid were added as catalyst. The mixtures were refluxed for 5–6 h, followed by cooling to room temperature. The resulting crystals were filtered under vacuum. Then, the products were recrystallized from absolute methanol.

2.2. Synthesis of the complexes

A solution of Cu(II) acetate and Co(II) acetate dihydrate in absolute ethanol was added to a solution of 4-4'-methylene

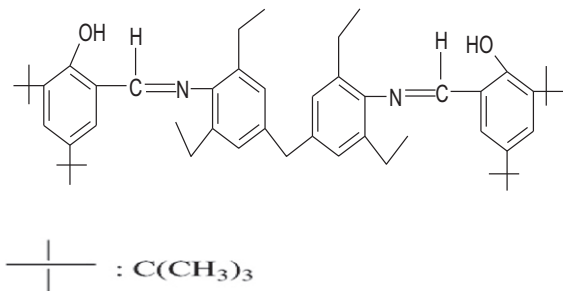


Fig. 1. Structures of 4-4'-methylene bis(2,6-diethyl)aniline–3,5-di-tert-butylsalicylaldimin ligand (MA:742).

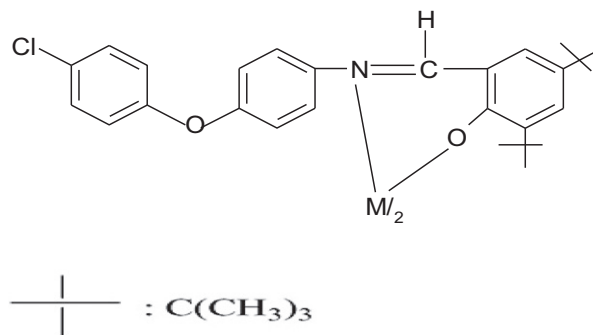


Fig. 2. Structures of 4-4'-methylene bis(2,6-diethyl)aniline–3,5-di-tert-butylsalicylaldimin ligand metal complexes ($\text{M:Co}_2\text{H}_2\text{O}$, Cu).

bis(2,6-diethyl)aniline–3,5-di-tert-butylsalicylaldimin ligand with equal molar amounts, according to the similar method reported in the literatures [36,37]. The stirred mixture was refluxed for 60 min. The volume was reduced to 15–20 mL and left to cool to room temperature. The compound was precipitated, filtered and washed with a small amount of methanol. The product was recrystallized in methanol and chloroform.

2.3. Catalyst preparation

The Co(II)–Cu(II) complex catalysts containing different percentages were prepared by mechanical mixing method. The prepared complex catalyst was used to hydrogen production by catalytic hydrolysis of NaBH_4 .

2.4. Generation of hydrogen

Hydrogen generation tests of NaBH_4 hydrolysis with the prepared complex catalysts were carried out in a 200 mL three-neck flask immersed in a water bath, which was described in details along with its experimental setup in our previous work [38]. The prepared Co(II)–Cu(II) catalyst was initially put at the bottom of the flask at a nitrogen atmosphere system. Hydrolysis reaction began when 10 mL solution including 2.5 wt% NaBH_4 –5 wt% NaOH was introduced into the flask. The theoretical hydrogen volume in this mixture according to Eq. (1) is about 685 mL at temperature of 30°C . A measured volume of released gas was subsequently converted into yield of produced hydrogen after the total amount of gas had been collected.

3. Results and discussion

3.1. Crystalline structures of complex catalysts

Figs. 3 and 4 show the XRD patterns of complex catalysts. These results show that metal complexes and complex mixtures indicate a crystalline nature, not an amorphous nature. It was observed that crystalline structure of complex catalysts was strongly affected by Co(II)–Cu(II) mixture ratio. The major peaks of complex mixture catalysts were generated at 4.54, 6.76, 8.32, 8.66, 10.16, 12.162, 14.132, 15.74, 17.44, 19.98, 20.62, 21.68, 23.60, 28.30 and 28.70° , corresponding to reflections at 256, 237, 129, 198, 232, 257, 256, 266, 263, 266, 316, 206, 274, 269 and 169, respectively, as illustrated in Fig. 3. The diffraction peaks of Co(II)–Cu(II) mixture became sharper and narrower with increasing mixture, indicating an increase in the crystal structure. It is interesting to note that these diffraction peaks of complex mixture catalysts did not correspond to either Cu or Co metal complexes. This is because Cu metal

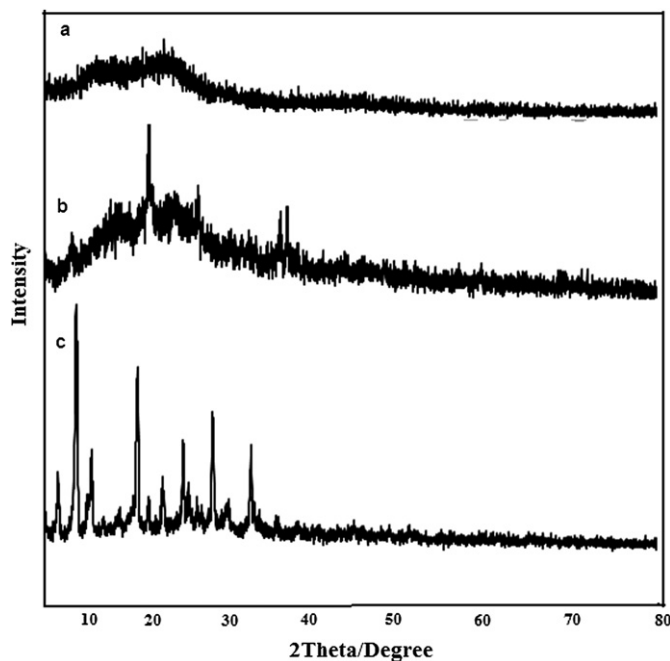


Fig. 3. X-ray diffractograms of (a) Co(II) metal complex (b) Cu(II) metal complex (c) 40 wt% Co(II)–60 wt% Cu(II) complex mixture.

complex and Co metal complex intimately interacted with each other during the mixture process. In addition, this indicates that the fine mixing occurred in the preparation of Co and Cu metal complex.

The XRD patterns of various Co(II)–Cu(II) mixture percentages are displayed in Fig. 4. The XRD patterns include the Co(II)–Cu(II)

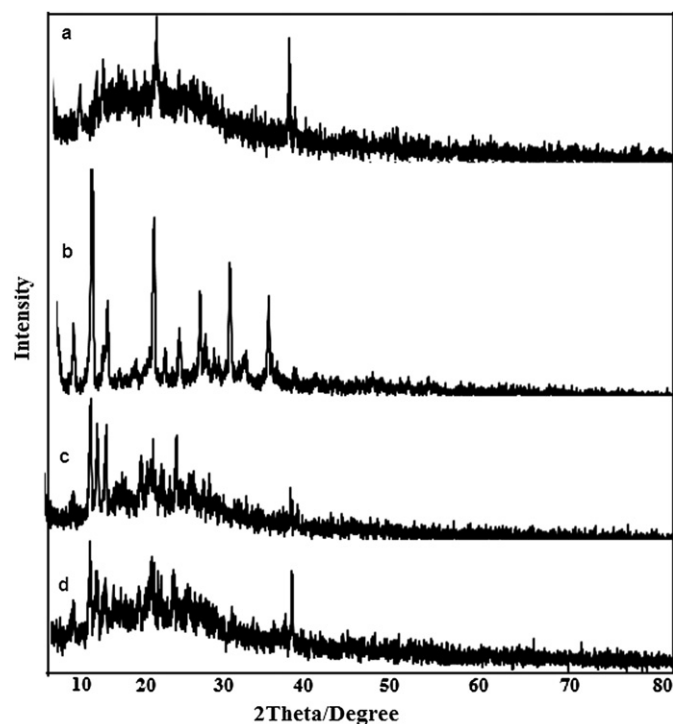


Fig. 4. X-ray diffractograms of (a) 30 wt% Co(II)–70 wt% Cu(II), (b) 40 wt% Co(II)–60 wt% Cu(II), (c) 60 wt% Co(II)–40 wt% Cu(II), 20 wt% Co(II)–80 wt% Cu(II) complex mixtures.

mixture percentages having 30:70 (a), 40:60 (b), 60:40 (c) and 80:20 (d) catalysts. As shown in Fig. 4(a) and (b), with the increase from 30:70 to 40:60 of Co(II)–Cu(II) mixture percentage, the new and sharper diffraction peaks were appeared. However, with the increase from 40:60 to 80:20 of Co(II)–Cu(II) mixture percentage, strength of diffraction peaks were gradually decreased. This indicates that there is a limitation of Co(II) or Cu(II) atoms that could be incorporated into the complex matrix. This means that excessive Co or Cu is prone to sintering at hydrolysis temperature of NaBH_4 . Moreover, the some peaks characteristic of Co(II)/Cu(II) complex catalyst almost completely disappeared (Fig. 4, patterns c, d). This indicates that some compounds or groups separate from the complex catalysts.

3.2. Scanning electron microscopy

SEM is used to assess the microscopic aspects of the complex catalysis. A typical SEM micrograph is as shown in Fig. 5a–d. The micrograph reveals that the Cu–Co complex mixture appears as crystalline particles with definite flower-like particles. The SEM of complex mixture shows big size uniform particles with the tendency to cluster together to form larger aggregates. This indicates a maximum or complete complex formation. In addition, the particle sizes ranged from submicrons to larger than $\sim 1 \mu\text{m}$.

3.3. FT-IR spectra

The FT-IR of complex catalysts has been studied in order to characterize their structures. Characteristic absorptions in the spectra FT-IR of their Cu(II), Co(II) metal complexes and Co–Cu metal complex mixture are represented in Fig. 6. The FT-IR spectra of complex catalysts are found to be very similar to each other. Hence, significant frequencies are selected by comparing the FT-IR spectra of the complex catalysts. Some of the fundamental peaks of Cu(II), Co(II) metal complex catalysts were shifted from its position after mixture (Fig. 6). The very strong and sharp bands located at $1618\text{--}1621 \text{ cm}^{-1}$ are assigned to the --CH=N stretching vibrations of the azomethine. On the Co–Cu complex mixture, this band is shifted to broader and a lower frequency range 1563 cm^{-1} . It might be due to the formation of active sites at the between of complexes by mixture treatment. As seen be that the spectra FT-IR of Cu(II), Co(II) metal complexes and mixture bands at between 2958 and 2874 cm^{-1} are due to the free --OH or intramolecular --OH...N groups. Two peaks at about 3342 and 3153 cm^{-1} for Cu(II) metal complex disappeared following mixture treatments. Peaks at about 1000 and 1100 cm^{-1} for Cu(II), Co(II) metal complexes converted to broad one peak following mixture treatment at about 1027 cm^{-1} for Co(II)–Cu(II) metal complex mixture corresponds to C–O stretching vibrations. In addition, the absorption bands in the 1720 and 1650 cm^{-1} for the Co(II) complex assigned to C=O stretching vibrations of ketones, aldehydes, lactones or carboxyl groups were disappeared following mixture treatments.

3.4. Effect of Co(II)–Cu(II) ratio

Co(II)–Cu(II) complex catalysts containing different Co(II)–Cu(II) percentages prepared by mechanical mixing method were tested for hydrogen production from NaBH_4 hydrolysis. Their hydrogen production conversions at 30°C are shown in Fig. 7. Firstly, the catalytic hydrogen performance volume is 520 mL for the 100% percentage of Cu(II) and 0% Co(II) complexes. The hydrogen volume decreases with the increase of mixture percentage of Co(II)–Cu(II) from 10:90 to 20:80. The hydrolysis of NaBH_4 is completed in the

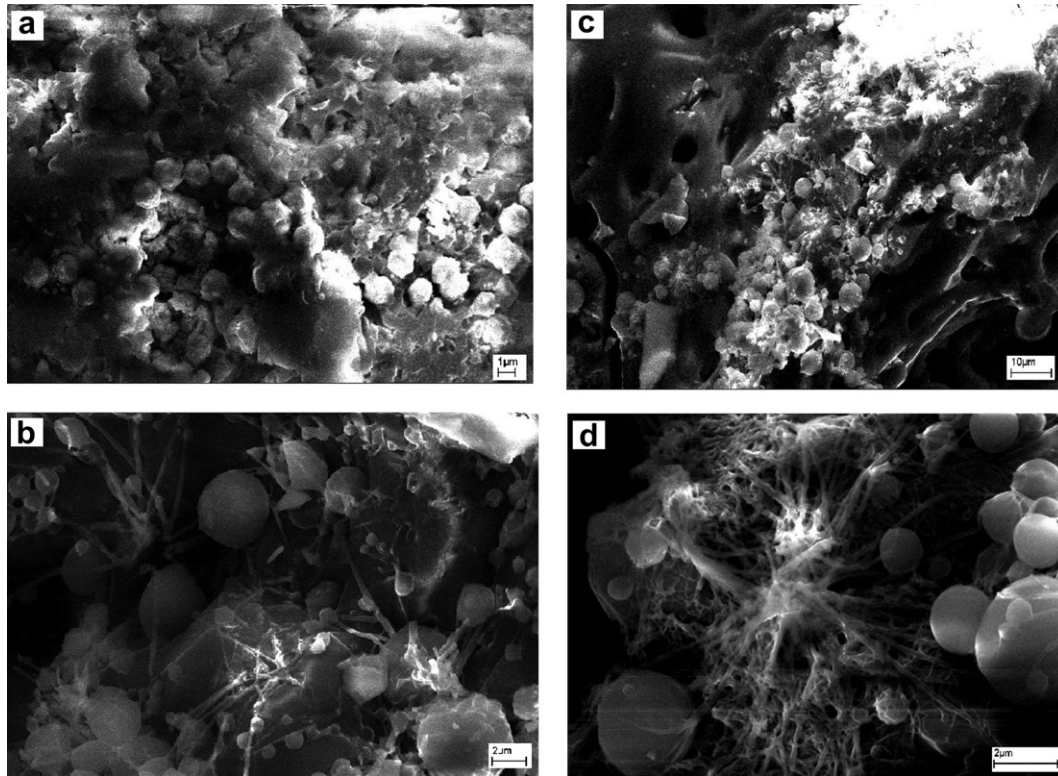


Fig. 5. (a–d) SEM images of 40 wt% Co(II)–60 wt% Cu(II) complex mixture.

time interval 9000 and 10,800 s with the increase of mixture percentage of Co(II)–Cu(II) from 10:90 to 20:80. Then, the catalytic hydrogen performance is increased with the increase of mixture percentage of Co(II)–Cu(II) from 20:80 to 40:60. The hydrolysis of NaBH_4 is completed in the time interval 10,800 and 6600 s with the increase of mixture percentage of Co(II)–Cu(II) from 20:80 to 40:60, which suggests that there is an optimum ratio of Co(II)–Cu(II) catalyst. However, it is completed in the time of 9000 s as 60:40 the Co(II)–Cu(II) mixture percentage further increases. The possible reason is the much Co or Cu could be agglomerated on the surface of

catalyst, which leads to a decrease in the metal surface area and, hence, a lower catalyst activity [39–41].

3.5. Effect of catalyst amount

To examine the effect of Co(II)–Cu(II) complex catalyst amount, the hydrogen generation yield was measured by hydrolysis of 2.5 wt% NaBH_4 + 5% NaOH solution using Co(II)–Cu(II) catalyst (15, 25, and 50 mg) at 30 °C. As observed in Fig. 8, the hydrogen generation yield was increased due to activation of the catalyst, as

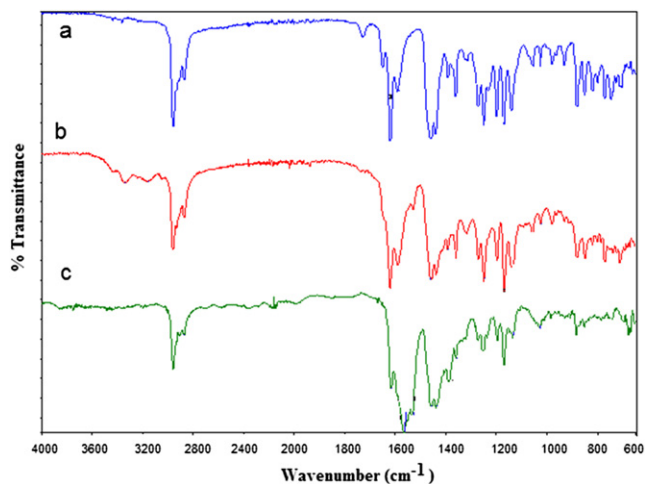


Fig. 6. FT-IR spectra of (a) Co(II) metal complex (b) Cu(II) metal complex (c) 40 wt% Co(II)–60 wt% Cu(II) complex mixture.

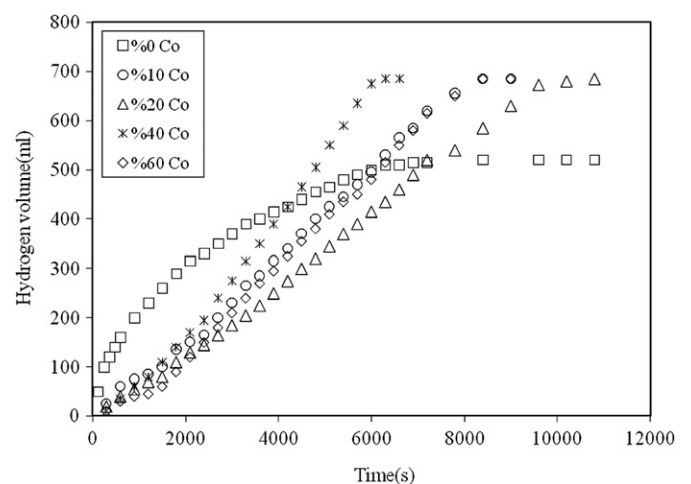


Fig. 7. Effect of Co(II)–Cu(II) catalyst ratio on the hydrogen generation rate at 30 °C, 2.5 wt% NaBH_4 , 5% NaOH and 25 mg of catalyst.

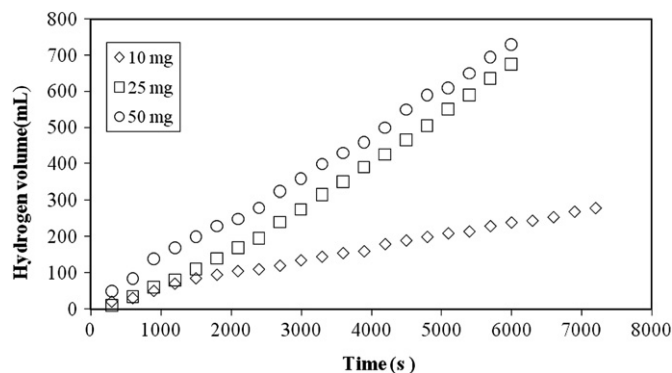


Fig. 8. Effect of catalyst amount on the hydrogen generation rate at 30 °C, 2.5 wt% NaBH₄, 5% NaOH and 40 wt% Co(II)–60 wt% Cu(II) complex mixture.

increasing from 15 mg to 50 mg the Co(II)–Cu(II) complex catalyst amount. These results show that hydrogen generation rate can be determined by controlling the catalyst amount.

3.6. Effect of NaOH concentration

Fig. 9 illustrates that the hydrogen generation rates changes with different NaOH concentrations, i.e. 1 wt%, 5 wt%, and 10 wt%, on hydrogen production rate at 30 °C in 2.5 wt% NaBH₄ solution with 25 mg of Co(II)–Cu(II) complex catalyst. As observed in Fig. 8, the hydrogen generation volume increases with increasing in NaOH concentration and reaches a maximum at 5-wt%, then decreases with further increasing in NaOH concentration. Ding et al. [42] reported a condition similar to ours with respect to NaOH concentration by using Co–CuB supported catalyst. They suggested that probable reason is that hydroxyl ion is involved in the hydrolysis of NaBH₄. In addition, they stated that excessive concentration of NaOH would lead to decrease of NaBO₂ solubility and the subsequent precipitation from the solution and adherence on the catalyst surface.

3.7. Effect of NaBH₄ concentration

Fig. 10 shows the effect of NaBH₄ concentration on the hydrogen generation rate. Effect of NaBH₄ concentration on the hydrogen generation rate was measured using x wt% NaBH₄ ($x = 1, 2, 5$ and 5), 5 wt% NaOH solutions at 30 °C. As can be seen in Fig. 9, as weight

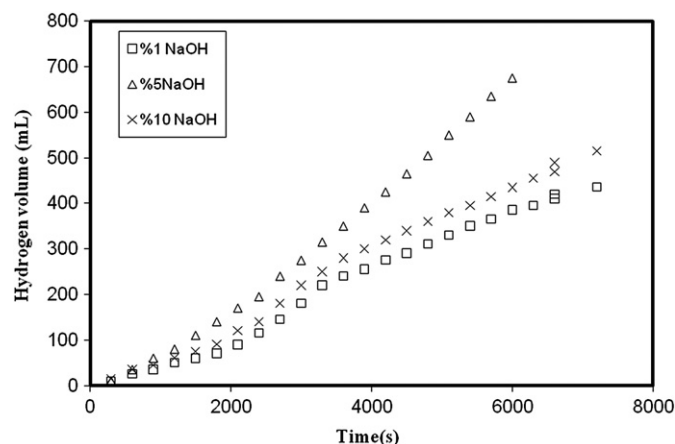


Fig. 9. Effect of NaOH concentration on the hydrogen generation rate at 30 °C, 2.5 wt% NaBH₄ and 25 mg of 40 wt% Co(II)–60 wt% Cu(II) complex mixture.

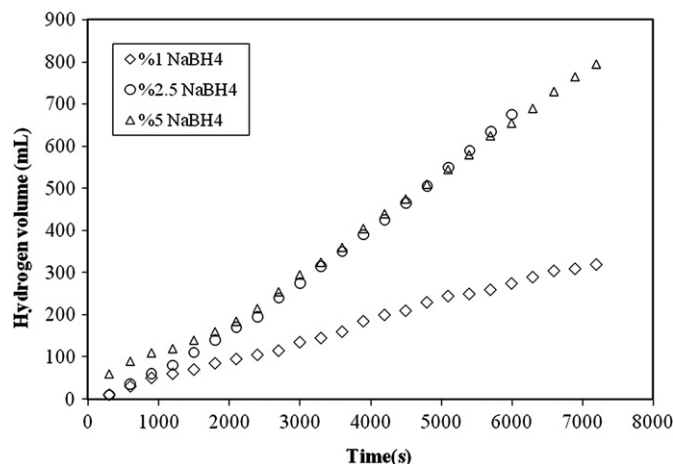


Fig. 10. Effect of NaBH₄ concentration on the hydrogen generation rate at 30 °C, 5% NaOH and 25 mg of 40 wt% Co(II)–60 wt% Cu(II) complex mixture.

percent NaBH₄ is increased, initial H₂ generation rates increase and reach a maximum with 2.5 wt% NaBH₄. Then, hydrogen generation rates at higher concentrations remained almost constant. The possibly reason is due to reduced solution viscosity, i.e. reduced mass transport allows more NaBH₄ and H₂O to contact catalyst surfaces, thereby affecting the hydrogen generation rate. The similar result to our study for the effect of NaBH₄ concentration on the hydrogen generation rate has been reported in the literatures [6] (Fig. 11).

3.8. Effect of the reaction temperature

Fig. 10 shows the hydrogen generation rate with 5% NaBH₄ aqueous solution at different temperature ranges of 25–60 °C. As known, the higher the hydrolysis temperature, the higher the hydrogen yields percentage and the shorter the hydrolysis time. However, the rate of hydrolysis decreases with the increase in temperature in our study. In general, transition metals have shown a good level of activity and selectivity for hydrogen production with hydrolysis of NaBH₄. The main problem found when using these catalysts is deactivation by sintering and carbon deposition due to the harsh conditions in the high temperatures [43]. Our results confirm that hydrogen production with hydrolysis of NaBH₄ on the complex catalyst is easier to catalyze at lower temperature.

Matthews et al. [44] reported a condition similar to ours with respect to temperature with the hydrolysis of NaBH₄ with saturated

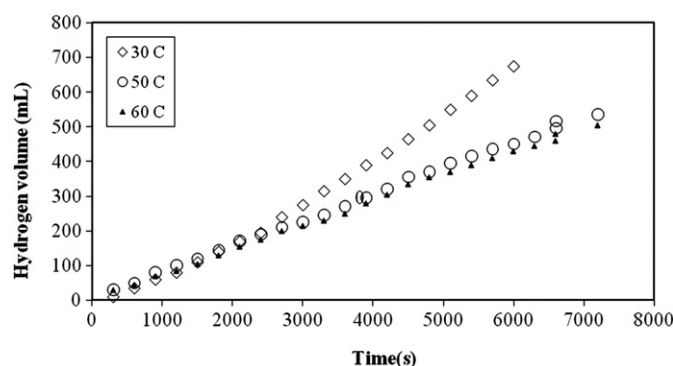


Fig. 11. Effect of temperature on the hydrogen generation rate at 2.5 wt% NaBH₄, 5% NaOH, and 25 mg of 40 wt% Co(II)–60 wt% Cu(II) complex mixture.

steam at temperatures from 383 to 413 K without a catalyst. At 383 K, they obtained the highest yields of hydrogen. They suggested that probable reason is the solid agglomerated products. Therefore, they proposed that the formation of an impermeable by-product shell during reaction at high temperatures limits the mass transfer of the steam to the reactant and reduces the rate of conversion.

4. Conclusions

Co(II)–Cu(II) supported salicylaldehyde derivatives complex catalysts and their mixtures with different Co(II)–Cu(II) ratios were prepared by a mechanical mixing method for hydrogen production by hydrolysis of NaBH₄. The hydrolysis of NaBH₄ with Co(II)–Cu(II) complex catalyst was investigated depending on the NaBH₄ concentration, NaOH concentration, temperature and catalyst amount. The catalytic performance was changed obviously with the variation of Co(II)–Cu(II) ratio. The optimal mixture percentage of Co(II)–Cu(II) was 40:60. However, it was declined hydrogen production ratio while the Co(II)–Cu(II) mixture percentage ratio further increases. The possible reason is the much Co or Cu could be agglomerated on the surface of catalyst, which leads to a decrease in the metal surface area and, hence, a lower catalyst activity. It was observed that crystalline structure of complex catalysts was strongly affected by Co(II)–Cu(II) mixture ratio. It can be concluded that the Co(II)–Cu(II) complex catalyst may be used for hydrogen generation by hydrolysis of NaBH₄.

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